1690 cm^{-1} that was assigned to the ketone C=O in the starting compound **3**; nmr δ 1.3 (3 H, t, CH_3 of Et), 2.1 (3 H, s, $COCH_3$), 3.1 (2 H, q, CH_2 of Et), 3.9 (12 H, m, 4 OCH_3), 5.0 (1 H, s, OH), 7.0–7.3 (5 H, m, ArH).

Anal. Calcd for $C_{24}H_{26}O_7$: C, 67.59; H, 6.15. Found: C, 67.70; H, 6.23.

1,3,4-Triacetoxy-2-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalene (**7**).—Reductive acetylation of the naphthoquinone **4** with zinc dust in acetic anhydride after the procedure described by Bentley[4] gave the triacetyl derivative **7**, mp 221–222°.

Anal. Calcd for $C_{28}H_{26}O_{10}$: C, 62.65; H, 5.26. Found: C, 62.63; H, 5.42.

An attempt to prepare **7** by oxidation of **3** by *m*-chloroperbenzoic acid led to 60% recovery of **3** and *m*-chlorobenzoic acid (83%) but, there was no evidence for the formation of **7**.

6-Acetylhomoveratric Acid (**9**).—3,4-Dimethoxyphenylacetic acid (15 g, homoveratric acid) was dissolved in warm acetic acid (25 ml) and the solution was stirred into polyphosphoric acid (200 g). After standing at room temperature for 2 days with occasional stirring, the reaction mixture was added to water (1500 ml) and the aqueous solution was extracted continuously with ether (1300 ml) for 18 hr. Evaporation of the ether extract left 12 g of colorless solid that after recrystallization from water (3 parts)–EtOH (1 part) had mp 175–176° (lit.[3] mp 175°). The identification of the product was by comparison with a sample prepared by Bentley's method and by oxidation to the known 3,4-dimethoxyhomophthalic acid.[3] Compound **9** could also be isolated in several crops from the water solution on long standing (1–3 weeks).

11-Acetoxy-6-methyl-2,3,8,9-tetramethoxychrysene (**10**).—A mixture of 6-acetylhomoveratric acid (**9**, 2 g) in pyridine (16 ml) and acetic anhydride (12 ml) was heated under reflux conditions for 1 hr. After standing for 12 hr, the red solution was added to 300 ml of 10% HCl solution and the crude product (1.8 g, mp 120°) was collected. Extraction of the solid with hot MeOH left a residue (0.75 g), mp 253–258°. The chyrsene derivative was purified by recrystallization from $CHCl_3$–petroleum ether: mp 263–265°; *m/e* 420 (M^+); ir 1750 cm^{-1} (C=O); uv λ_{max}^{EtOH} 231 nm (log ε 4.81), 259 sh (4.60), 279 sh (5.02), 287 (5.15), 307 (4.54), 319 (4.34), 334 (4.26), 362 (4.00), 380 (4.08); nmr δ 2.51 (3 H, s, CH_3), 2.75 (3 H, s, CH_3CO), 4.14 (12 H, m, OCH_3), 7.20–8.75 (6 H, m, ArH).

Anal. Calcd for $C_{25}H_{24}O_6$: C, 71.42; H, 5.75. Found: C, 71.09; H, 5.70.

Registry No.—1, 26954-85-8; 2 30034-55-0; 3, 40940-67-8; 4, 40940-48-5; **5b**, 40940-49-6; **7**, 40940-50-9; **8a**, 40940-51-0; **9**, 38210-84-3; **10**, 40940-53-2; homoveratric acid, 93-40-3.

A Convenient Preparation of Tetrahydrofurylidene Acetates

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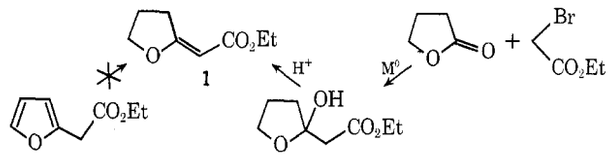
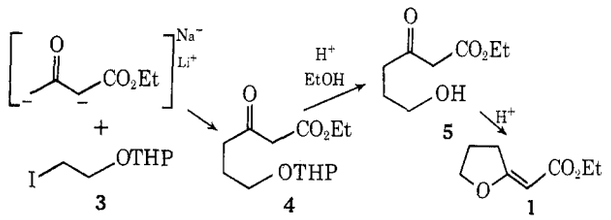
Recent heterocyclic studies have required reduced derivatives of furan for synthetic building blocks. This had led to a convenient preparation of ethyl α-(tetrahydro-2-furylidene)acetate (**1**) by a novel epoxide ring cleavage. The preparation of this compound (**1**) by the reduction of furan esters seemed unlikely. The reaction of organometallics with γ-butyrolactone proved to be a complex process but did, on treatment with acid, afford furylidene acetate **1** in 24% yield from γ-butyrolactone.[1] Use of the dianion of ethyl acetoacetate (**2**), following the procedure of Weiler,[2]

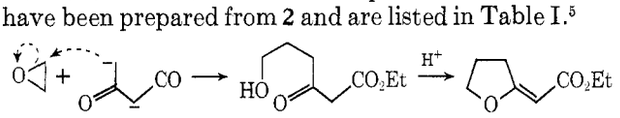


proved a very simple approach to the formation of the carbethoxymethylene tetrahydrofuran **1**.



Initially, the dianion of ethyl acetoacetate (**2**) was alkylated with the tetrahydropyranyl ether (THP) of iodoethanol (**3**), forming a new β-keto ester, **4**, alkylation occurring at the methyl rather than methylene position of ethyl acetoacetate. This was converted into **1** in 34% yield (from ethyl acetoacetate) by treatment with first aqueous ethanol and acid (**4** → **5**) and then benzene and *p*-toluenesulfonic acid (**5** → **1**). The same alkylation procedure with the THP of chloro- or bromoethanol failed to yield keto ester **4** in any usable quantities.

Improvement in the preparation of ester **1** was facilitated by the discovery that the dianion of ethyl acetoacetate (**2**) would undergo smooth epoxide ring opening[3] in a manner analogous to the above-cited alkylation reaction (bond formation occurring at the methyl position of ethyl acetoacetate). When approximately 1 equiv of ethylene oxide was added to litho sodio ethyl acetoacetate (**2**) a crude alcohol **5** was formed which was readily transformed into tetrahydrofuran **1** on treatment with oxalic acid in methylene chloride (54% yield). The generality of this novel dianion epoxide ring opening and enol etherification is apparent from the reduced furan and thiophene derivatives that have been prepared from **2** and are listed in Table I.[5]



The product of initial epoxide (sulfide) ring opening (*i.e.*, **5**) was never purified. However, the spectral data (ir, nmr) from these crude products, **5**, and the analogous compounds from propylene oxide and butylene oxide (propylene sulfide) suggest these alcohols (mercaptans) could be isolated and used for synthetic transformations other than simple intramolecular enol etherification.

The stereochemistry about the double bond of these esters is as shown in Table I (E or trans). This is apparent from shift reagent studies which confirm the close proximity of the ester carbonyl and allylic, methylene ring protons. That is, assuming proton deshielding decreases as the intramolecular distance

(1) F. F. Blick and B. A. Brown, *J. Org. Chem.*, **26**, 3685 (1961), and references cited therein.

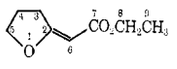
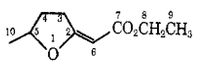
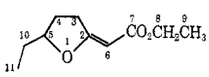
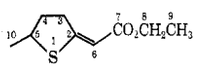
(2) L. Weiler, *J. Amer. Chem. Soc.*, **92**, 6707 (1970); L. Weiler, *Tetrahedron Lett.*, 4809 (1971).

(3) For examples of sodio ethyl acetoacetate epoxide ring opening see ref 4; to our knowledge this study represents the first report of a dianion epoxide ring cleavage.

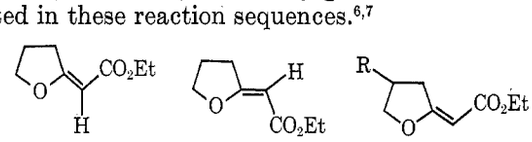
(4) A. Graham, A. Millidge, and D. Young, *J. Chem. Soc.*, 2180 (1954); T. Temnikova, G. Markina, V. Borodavko, and N. Yaskina, *Zh. Org. Khim.*, **6**, 739 (1970); G. El Naggar and B. Ershov, *ibid.*, **5**, 1368 (1969).

(5) All products were characterized by ir, nmr, uv, mass spectra and C, H analysis.

TABLE I

Product	Epoxide (sulfide) used	Bp, °C (0.5 mm)	Yield from ethyl acetoacetate, %
 1		55	54
 6		80	62
 7		100	60
 8		120	57

to the shift reagent increases and that this reagent coordinates on the ester carbonyl oxygen, it follows that isomer **1**, and not **9**, is the only geometrical isomer isolated in these reaction sequences.[6,7]



1 **9** **10**, R = Me or Et

Unsymmetrical epoxides (sulfides) were employed in this study to ascertain the direction of ring opening. In the reactions attempted, the least hindered attack lead to the products (**6**, **7**, and **8**) isolated and shown in Table I. The isomeric enol ether **10** (above) has not been detected by glc, lc, nmr-shift reagent, or ^{13}C studies. However, the yields of **6**, **7**, and **8** do not preclude the formation of such isomeric compounds.

Shift reagents were again employed to clearly show the methine proton resonance (C_5, see Table I for numbering) in compounds **6** and **7** and the absence of any methylene proton resonances that would be observed if isomeric compound **10** (R = Me or Et) were present.[6] In addition, the ^{13}C-proton decoupled nmr of furylidene **6** exhibited single resonances for C_5 and C_8 at the chemical shift expected confirming the homogeneity of this sample.[8] Studies related to the reactivity of these systems are now underway.

Experimental Section

General Method.—The dianion of ethyl acetoacetate was prepared in THF using Weiler's procedure.[2] To this was added the epoxide or sulfide (1.1 equiv) at 0° and the reaction mixture was immediately brought to room temperature. After 3 hr, water (10 ml/10 mmol of dianion) was added, then dilute HCl (aqueous 5%) until the mixture was neutral to weakly basic. This was extracted with ether (three times), and the combined organic phases were washed with saturated, aqueous sodium bicarbonate and brine and dried over sodium sulfate. The volatiles were removed *in vacuo* and the residue was combined with an equal weight of oxalic acid in methylene chloride (50 ml/g of residue) and heated under reflux for 2 hr in an inert atmosphere. After cooling, this mixture was washed with water, sodium bicarbonate (saturated, aqueous), and brine (saturated, aqueous) and dried over sodium sulfate. The volatiles were removed *in vacuo;* the residue was distilled at reduced pressure. (Glc, 5-ft 10% SE-30, 155–175°, and lc, Lichrosorb, cyclohexane–THF elution, analyses were conducted on all carbethoxymethylene compounds.)

Ethyl α-(Tetrahydro-2-furylidene)acetate (1).—Ethylene oxide (~2.2 g, 0.05 mol) was added to the dianion of ethyl acetoacetate (0.05 mol) in the manner described above. This afforded 4.6 g of **1**: 54%; λ_{max}^{film} 1701, 1642 cm^{-1}; λ_{max}^{EtOH} 245 nm (ε 13,400); pmr in $\delta_{TMS}^{CCl_4}$ 5.06 (t, J = 0.4 Hz, 1, C-6 H), 4.08 (t, J = 7.0 Hz, 2, C-5 H's), 3.95 (q, J = 7.0 Hz, 2, $-O-CH_2-CH_3$), 3.00 (m, 2, C-3 H's), 2.01 (m, 2, C-4 H's), 1.18 (t, J = 7.0 Hz, 3, $-OCH_2CH_3$); 156 (*m/e*); bp 50° (0.05 mm); cmr in ppm_{TMS}^{neat} 176.6 (C_2, see Table I for numbering), 167.5 (C_7), 89.0 (C_6), 71.8 (C_5), 58.8 (C_8), 30.2 (C_3), 23.6 (C_4), 14.5 (C_9).

Anal. Calcd for $C_8H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.31; H, 7.11.

Ethyl α-(Tetrahydro-5-methyl-2-furylidene)acetate (6).—The dianion of ethyl acetoacetate (0.05 mol) and propylene oxide (2.91 g, 0.05 mol) afforded 5.27 g of **6**: 62%; λ_{max}^{film} 1701, 1645 cm^{-1}; λ_{max}^{EtOH} 245 nm (ε 13,400); pmr in $\delta_{TMS}^{CCl_4}$ 5.04 (t, J = 0.4 Hz, 1, C-6 H), 4.26 (m, 1, CH_3CHO-), 3.82 (q, J = 7.2 Hz, 2, $-OCH_2-CH_3$), 2.87 (m, 2, C-3 H's), 1.97 (m, 2, $-CHCH_2CH_2-$), 1.17 (d, J = 7.0 Hz, 3, C-5 H), 1.04 (t, J = 7.2 Hz, 3, $-OCH_2CH_3$); 170 (*m/e*); bp 80° (0.05 mm); cmr in ppm_{TMS}^{neat} 176.1 (C_2), 167.5 (C_7), 89.0 (C_6), 80.3 (C_5), 58.3 (C_9), 31.1 (C_3), 30.6 (C_4), 20.1 (C_8), 14.3 (C_{10}).

Anal. Calcd for $C_9H_{14}O_3$: C, 60.74; H, 8.92. Found. C, 60.79; H, 8.99.

Ethyl α-(Tetrahydro-5-ethyl-2-furylidene)acetate (7).—The dianion of ethyl acetoacetate (0.05 mol) with 1,2 butylene oxide (3.60 g, 0.05 mol) afforded 5.52 g of **7**: 60%; λ_{mxx}^{film} 1709, 1645 cm^{-1}; λ_{max}^{EtOH} 245 nm (ε 13,500); pmr $\delta_{TMS}^{CCl_4}$ 5.04 (t, J = 0.4 Hz, 1, C-6 H), 4.14 (m, 1, C-5 H), 3.97 (q, J = 7.4, 2, $-OCH_2CH_3$); 2.95 (m, 2, C-3 H's), 2.00–1.62 (m, 4, C-4 H's and C-10 H's), 1.21 (t, J = 7.0, 3, CH_3CH_2-), 1.10 (t, J = 7.4, 3, $-OCH_2CH_3$); 184 (*m/e*); bp 100° (0.05 mm).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.38; H, 8.72.

Ethyl α-(Tetrahydro-5-methyl-2-thiophenylidene)acetate (8).—The dianion of ethyl acetoacetate (0.048 mol) with propylene sulfide (3.56 g, 0.048 mol) afforded 5.20 g of **8**: 57%; λ_{max}^{film} 1709, 1645 cm^{-1}; λ_{max}^{EtOH} 288 (ε 13,500); pmr δ_{TMS}^{CCl} 5.70 (t, J = 0.4 Hz, 1, C-6 H), 4.06 (q, J = 7.0 Hz, 2, $-OCH_2CH_3$), 3.58 (m, 1, C-5 H), 2.81 (m, 2, C-3 H's), 2.18 (m, 2, $-CHCH_2CH_2-$), 1.37 (d, J = 6.5 Hz, 3, CCH_3), 7.23 (t, J = 7.0 Hz, 3, $-OCH_2CH_3$); 1.86 (*m/e*); bp 120° (0.05 mm).

Anal. Calcd for $C_9H_{14}O_2S$: C, 58.05; H, 7.58. Found: C, 58.17; H, 7.47.

Acknowledgments.—This work was supported by the American Cancer Society Grant No. IC-83.

Registry No.—**1**, 40954-14-1; **6**, 40954-15-2; **7**, 40954-16-3; **8**, 40954-17-4;e thylene oxide, 75-21-8; litho sodio ethyl acetoacetate dianion, 40902-62-3; propylene oxide, 75-56-9; 1,2-butylene oxide, 106-88-7; propylene sulfide, 1072-43-1.

(6) The shift reagent used was trisdipivalomethanatoeuropium(III) or Eu(DPM)$_3$.

(7) H. M. McConnell, R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958), and references cited therein.

(8) The predicted and observed ^{13}C chemical shift of compound **6** are within experimental error based on model acrylate and tetrahydrofuran systems, as well as the parent unsubstituted furylidene **1**.

The Orientation in Alkaline Halogenation of 2-Butanone

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In a recent communication[1] the products of reactions of 2-butanone (I) and its 1-bromo (II) and 3-bromo

(1) C. G. Swain and R. P. Dunlap, *J. Amer. Chem. Soc.*, **94**, 7204 (1972).